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## (54) Improving the sputter deposition of metal-sulphur coatings

(57) An unbalanced magnetron sputter ion plating system (10) has a first magnetron (16 with a first target (18) of metal sulphide (eg  $\text{MoS}_2$  or  $\text{WS}_2$ ) and a second magnetron (20 with a second target (22 of metal (eg Titanium). In order to recover water and sulphur impurities from the surfaces of the coating chamber the metal target is energised in a pre-coating ion cleaning operation. Metal atoms getter the impurities and allow for better coatings, especially low friction  $\text{MoS}_2$  coatings. The coatings have low friction, good adhesion, and high hardness. Other hexagonal layer lattice materials other than sulphides may be deposited and in a further embodiment an article is described having a multi-layer coating  $\text{X}/\text{Y}/\text{X}/\text{Y}$  where X is one of i) a layer of hexagonal layer lattice material or ii) a layer of metal (reactive or non-reactive) or semi-metal (eg carbon) or a mixture or alloy having in it a metal or semi-metal; and where Y is the other of i) or ii). Apparatus for achieving these multi-layer coatings is also disclosed.

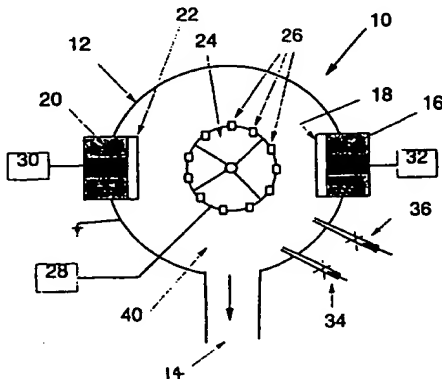


FIG. 1

GB 2 303 380 A

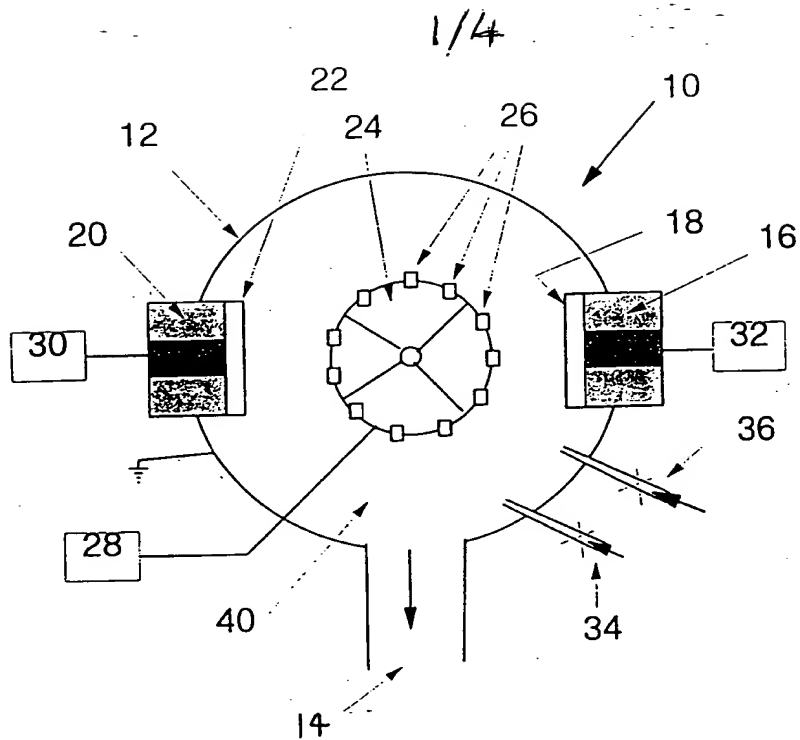


FIG. 1

## Reciprocating test on previous MoS<sub>2</sub>

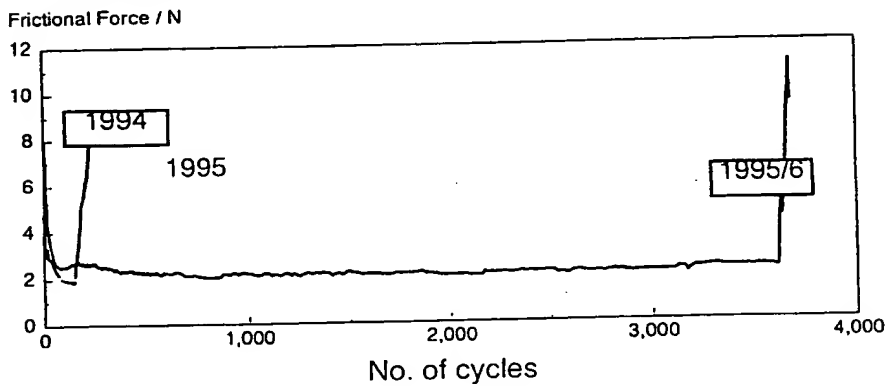


FIG. 2

2/4

## Reciprocating test on our new MoS<sub>2</sub>

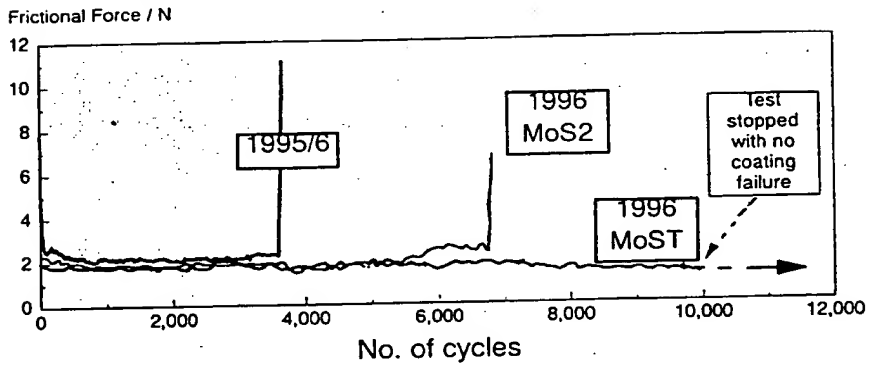


FIG.-. 3

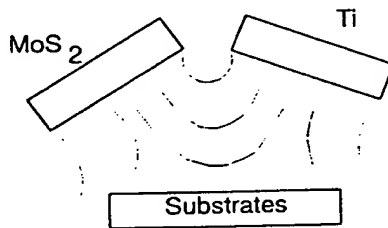


FIG. 4

3/4

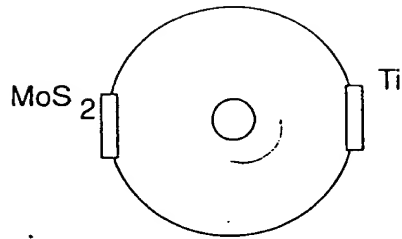


FIG.- 5 A

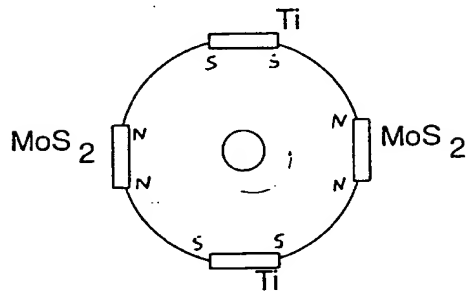


FIG. 5 B

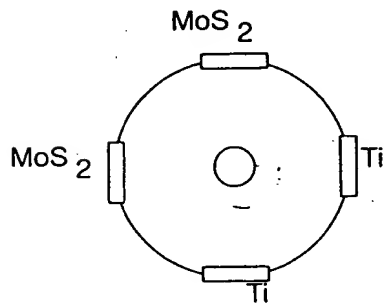


FIG.- 5C

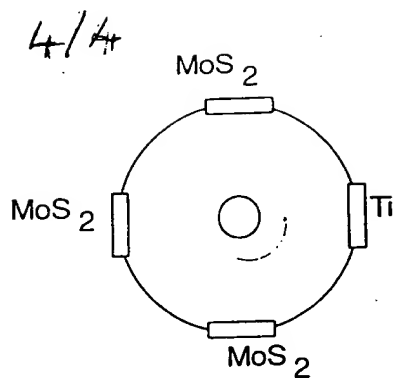


FIG.- 6

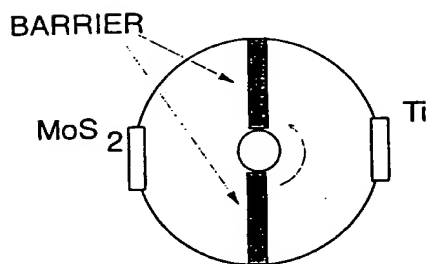


FIG.- 7

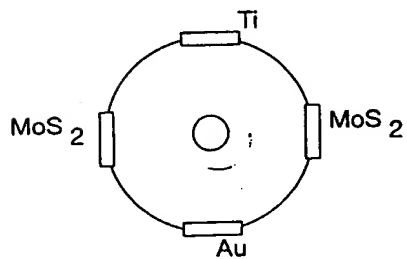


FIG. 8

IMPROVEMENTS IN AND RELATING TO  
METHODS FOR IMPROVING THE SPUTTER DEPOSITION OF  
METAL-SULPHUR COATINGS, E.G. MOLYBDENUM DI  
SULPHIDE ( $\text{MoS}_2$ ) COATINGS AND TO IMPROVED COATINGS

5

This invention relates to improvements in techniques for depositing coatings, such as metal-sulphur coatings, for example  $\text{MoS}_2$  and/or  $\text{WS}_2$  coatings, and also relates to coatings with improved properties.

10

$\text{MoS}_2$  coating have been used as solid lubricants in a variety of applications, but mostly as coatings on bearings in aerospace applications.

15

More recently,  $\text{MoS}_2$  coatings have been used to improve the efficiency of cutting tools. (German Patents 982616, or DE 2 345 355, and 4414051 C1, U.S. Patent Application 07 946 642, and Swiss Patent Application 2893/91).

20

$\text{MoS}_2$  coatings can be deposited by various methods but the preferred method is sputtering. In the past  $\text{MoS}_2$  coatings deposited by sputtering have been poorly adhered, of low density, with columnar structure, and the basal planes have been oriented normal to the substrate surface.

25

Recent developments at Teer Coatings using Closed Field Unbalanced Magnetron Sputter Ion Plating (CFUMBSIP) have produced  $\text{MoS}_2$  coatings of improved quality. In particular, the coatings are highly adherent, have a dense structure and the basal planes are oriented parallel to the substrate surface. These coatings have the properties required for good tribological performance.

30



Our earlier patent application EP 0 521 045 discloses a closed field unbalanced Magnetron Sputter ion plating system suitable for performing the present invention, and its contents are hereby incorporated by reference. The reader is directed to read EP 0 521 045 now to appreciate the disclosure incorporated. ("Closed Field" Magnetron Sputter Ion plating is the use of flux linking between adjacent magnetrons to provide a closed magnetic field between them, reducing the number of ionising electrons that escape from the system).

10 It has been found in practice that when using the sputtering method the results can be variable and that good coatings can be produced in one deposition sequence but that in another deposition sequence which is intended to be identical a coating with inferior properties is deposited.

15 We have linked this variability with the condition of the coating system and the condition of the  $\text{MoS}_2$  sputtering target, and in particular with the presence of contaminants in the deposition system. Two contaminants causing problems are water vapour from the atmosphere and Sulphur which is present in the chamber from previous  $\text{MoS}_2$  depositions.

20 The source of water contamination is the humidity in the atmosphere. This can be absorbed on all surfaces within the coating chamber but in particular is readily absorbed by the  $\text{MoS}_2$  sputtering target.

Sulphur may also be present in the sputtering chamber following previous coating operations and can form compounds such as  $\text{H}_2\text{S}$  which also contribute to contamination. The water vapour and/or the sulphur in the sputtering chamber can cause contamination on the substrate surface prior to deposition leading to coatings with poor adhesion. Water vapour and/or sulphur compounds can also cause contamination during coating.

30 The contaminants can lead to coatings with less desirable properties. For

instance brittle coatings may be deposited due to the presence of contaminants.

5 The aims of the present invention are two-fold: firstly to eliminate or reduce contamination so that coatings of a consistently high quality are deposited, and secondly to improve the coating properties.

10 The basis of the new method is the use of a second sputter target (or targets) as well as the metal/sulphur target (or targets) (e.g. metal sulphide such as  $\text{MoS}_2$  or  $\text{WS}_2$ ).

15 According to a first aspect of the invention we provide a sputter system having a first target of hexagonal layer lattice material, for example metal sulphide (e.g.  $\text{MoS}_2$  or  $\text{WS}_2$ ) and a second target of metal, the system being capable of being activated in a cleaning operation in which the second target is energised.

20 The target (or targets) can be of any metal but is preferably a highly reactive metal such as Titanium. In the following a titanium target is referred to. The sputter electrodes can be simple diodes, RF electrodes or magnetrons, but magnetron electrodes are preferred.

25 During the ion cleaning of the substrates which normally precedes the deposition process in the ion plating technique, we introduce the concept of energising the second target of (eg) Titanium.

We energise the titanium target for two reasons. Firstly in order to be able to strike an intense discharge to the substrates at a low argon pressure so that we ion clean the substrates efficiently at low argon pressure. Secondly we energise the Ti target to mop up the water vapour which is absorbed by the  $\text{MoS}_2$  target and also by the  $\text{MoS}_2$  previously deposited on the chamber walls, and the sulphur compounds (eg  $\text{H}_2\text{S}$ ) which remain in the chamber following previous depositions. This mopping up or gettering of the water vapour and sulphur compounds during the ion cleaning part of the process helps to create very good adhesion between coating and substrate. It also reduces contamination during deposition which can cause brittleness and other undesirable properties.

We obtain an improvement in the adhesion of the coating which is a function of the ion cleaning.

Since making the present invention we have become aware of some prior art (the results of an EPO search). The results of the search support the inventiveness of the present invention.

JP 3 014 227 is perhaps the most relevant document. This discloses a method of making semiconductor devices (a different field from low-friction coatings) in which a titanium target is energised in an argon atmosphere cleaning stage of operation. The Argon atmosphere is cleaned in the sputtering chamber prior to sputtering on to an aluminium substrate. The document is concerned solely with purifying the argon gas, not the aluminium target (aluminium is not a source of contamination). In our invention the target to provide the coating ( $\text{MoS}_2$ ) is a cause of the water vapour problem and a source of sulphur

contamination. JP 3014227 does not have an ion cleaning stage of the system to bombard the substrate to be coated with ions prior to coating. It is not even an ion plating system (just sputtering, no ion plating acceleration of ions onto the substrate).

5

The aluminium alloy of JP 3014227 is not a layer lattice and there is no question of arranging for parallel basal plane orientation of the coating (as we achieve - see later).

10

JP3014227 does not envisage cleaning the substrate to be coated and the target of coating material with ion cleaning (prior to ion plating the substrate) in order to remove impurities associated with the target. Moreover, it does not suggest using its Titanium target to reduce the argon pressure necessary to ion clean (it does not ion clean).

15

DE-C- 4414051 discloses a sputtering technique in which  $\text{MoS}_2$  is deposited on an interlayer of either  $\text{Cr}_3\text{Si}$  or Cr. It does not discuss ion cleaning or ion plating. It does not have a second target of metal (eg Titanium).

20

DD-A-202898 discusses depositing  $\text{MoS}_2$  on cutting tools, but does not discuss using a second metal target in impurity gettering stage, prior to ion cleaning a substrate before ion plating it.

25

DE-A-3516933 recognises that the presence of water vapour in the argon atmosphere is deleterious and describes a way of removing it from the gas atmosphere, but is not concerned with removing impurities from a plating chamber.

JP-A-03097855 shows a way of purifying argon gas prior to introducing to its sputter chamber. If used on MoS<sub>2</sub> systems the purified argon gas would only be re-contaminated when it was introduced into the sputter chamber (because the MoS<sub>2</sub> in the chamber has water vapour impurities, and other sulphur impurities would exist in the chamber). JP-A-03097855 shows that although a problem had been appreciated they had not thought of the present invention. Its effect is similar to De-A-3516933 in this respect.

10 EP-A-0534905 is equivalent to CH2893/91 referred to earlier, and merely discusses the desirability of MoS<sub>2</sub> coatings. It has little relevance to the present invention which is concerned with being able to provide good coatings with repeatability and fewer inconsistencies.

15 US-A-5002798 is concerned with depositing MoS<sub>2</sub> coatings, but was a totally different technique: it is not magnetron sputter ion plating.

FR-A-2586430 discusses the desirability of low friction coatings on articles such as skis, and using vapour phase deposition techniques, but  
20 does not discuss magnetron sputter ion plating, or ways of reducing impurities in MoS<sub>2</sub> coatings.

According to a first aspect of the invention we provide a sputter system having a first target (or targets) of metal sulphide (e.g. MoS<sub>2</sub> or  
25 WS<sub>2</sub>) and a second target (or targets) of metal.

Preferably the first target is a metal disulphide. It could be any hexagonal layer lattice material.

30 Preferably the metal second target is made of titanium.

The first and second targets are each separately energisable (e.g. each have their own associated magnetron, which have independently controllable power supplies).

5

Preferably the arrangement is such that the system is capable of being activated in a cleaning operation in which the second target is energised. The first (e.g.  $\text{MoS}_2$ ) target can be energised but is preferably not energised during the ion cleaning operation.

10

Preferably the first target comprises a magnetron with a target element, as may the second target. The, one, or both, magnetrons may be unbalanced.

15

In a MSIP system the cleaning operation involves the bombardment of the substrates by ions (usually argon ions) and in the new arrangement also involves the bombardment of the second target with ions so as to produce metal neutrals and ions in the sputter chamber, the metal neutrals and ions react with any impurities in the atmosphere of the chamber so as to remove them from the atmosphere. The metal neutrals and ions may adhere to the walls of the chamber. For example, water and sulphur in the coating chamber atmosphere react with the metal, preferably titanium, created from the second target, to form stable and non-contaminating compounds, during the cleaning operation. The ion bombardment, and the metal atmosphere created in the cleaning operation, help to react deposits of impurities left over from earlier coating operations. This improves the efficiency of the ion cleaning of the substrate and improves the quality of coating that is laid down.

20

25

According to a second aspect of the invention we provide a method of improving the sputter deposition of hexagonal layer lattice material, for example  $\text{MoS}_2$ , coatings comprising operating a sputter system in cleaning operation prior to a coating operation, the sputter system having a first  
5 target of material to be coated onto a substrate, and a second, cleaning, target of metal, and in which in the cleaning operation the second target is energised to produce a flux of reactive cleaning metal which reacts with impurities in the sputter chamber so as to remove them from having an active presence during the subsequent coating operation in which the first  
10 target is energised.

At least some of the reactive cleaning metal may be ionised metal, but the metal is not necessarily ionised. It could simply be sputtered metal. In one embodiment the reactive cleaning metal is partially ionised  
15 (perhaps about 5% ionised).

Preferably the second target is titanium or alternative reactive metal.

20 The first and/or second targets may have a respective associated magnetron.

The method may include having some of the metal of the second target incorporated into the layer that is deposited on the substrate to be  
25 coated.

The method may include introducing to the sputter chamber in the coating operation a further material which is incorporated in the coating. The further material is preferably gaseous at its point of introduction and  
30 may be nitrogen, or oxygen, or a hydrocarbon gas.

Water and/or sulphur in the sputter chamber atmosphere reacts with the metal, preferably titanium, created from the second target to form stable and non-contaminating compounds during the cleaning operation.

5

According to a third aspect of the invention we provide an article coated using the system of the first aspect of the invention, or using the method of a second aspect of the invention.

10

The basal planes of the metal sulphide layer (eg  $\text{MoS}_2$ ) are preferably parallel, or substantially parallel, to the surface of the substrate that they coat.

15

According to a fourth aspect the invention comprises the use of a second target of metal in a cleaning operation of a sputter system so as to reduce impurities in a low-friction coating subsequently produced from the system.

20

According to another aspect the invention comprises the use of a second metal target in a cleaning operation of a sputter system for the production of a low friction metal-sulphur, e.g.  $\text{MoS}_2$ , coating with improved mechanical properties.

25

Preferably the coating is between  $0.1\mu\text{m}$  and  $10\mu\text{m}$  thick, preferably about  $1\mu\text{m}$  thick.

30

According to another aspect of the invention we provide a method of reducing impurities when using a magnetron sputter ion plating system to coat an article with a metal sulphide coating having a target of metal sulphide to produce the coating and a second, different, metal target, and



energising the second target in a cleaning operation before coating commences, the second target a) producing reactive metal neutrals and ions which getter impurities in the ion plating chamber and also b) facilitating the generation of an intense discharge at low inert gas pressure  
5 ( in the ion plating chamber) to achieve better ion cleaning of the substrate to be coated than would be achieved if there were no energised second target.

According to a further aspect of the invention we provide a method  
10 of reducing contamination of a coating laid down by a magnetron ion plating system on a substrate using a first target of material to be deposited that attracts impurities (e.g. water vapour) comprising ion cleaning the substrate and the first target in an ion cleaning operation, prior to a deposition/coating operation, and wherein in the ion cleaning  
15 operation a second target of good gettering material is energised to create gettering neutrals or ions of said material which ions or atoms clean the system.

According to another aspect of the invention we provide a coating  
20 system comprising a first sputter source and second sputter source, the first and second sputter sources being arranged close to each other so that they can sputter simultaneously on to substrates situated in front of the two sputter sources, the first and second sources being of different materials so as to produce coating fluxes of different materials that  
25 deposit on to the substrates simultaneously to produce a coating of an approximately homogeneous mixture of the two materials on the substrates.

Figure 4 schematically illustrates such a system.

The substrates can be on a moving holder so that they are brought into and moved out of the coating position. The movement is preferably rotary.

5        According to a further aspect of the invention we provide a coating system comprising of a first sputter source and a second sputter source, the first and second sputter sources being so arranged that they are not close together, the sputter sources being of different materials, and a  
10        substrate holder being adapted to move during deposition so that the substrates are moved closer to and further away from each sputter source in turn, so that the substrates receive a coating flux from each of the sputter sources in turn so that the coating is not a homogeneous mixture of the two materials but consists of layers of varying compositions.

15        The substrate holder movement is preferably rotary (e.g. as shown in Figure 5) in which case a multi layer coating is deposited. Alternatively the substrate holder can reciprocate between the two sources.

20        It has been found that the coatings produced by the above described methods have a coefficient of friction that is consistently below 0.1, and frequently as low as 0.02.

25        According to another aspect of the invention we provide a method of producing an article with good tribological properties comprising providing the article with a coating having a plurality of layers X/Y/X/Y, and possibly more alternating layers, where Y is a low friction material, and X is a metal, semi-metal, or alloy or mixture of metal or semi-metal. Y may be a hexagonal layer lattice material. X may be a reactive metal,  
30        or a non reactive metal (eg gold or platinum).

Of course, we may start with a layer of X or Y. We would usually have the first layer or an article as the metal (or semi-metal) layer.

5 We also seek protection for a coated article having such layers X/Y/X/Y.

The layers of X and Y may be separated by one or more layers Z of a different material(s) (XYZ/XYZ/XYZ).

10

According to another aspect of the invention we provide a method of achieving in a magnetron sputter apparatus a layered coating having layers of a first kind and layers of a different, second kind, the method comprising having a first target source of one material and a second target  
15 source of a second material and moving the substrate to be coated so as to vary its distance from the first and second targets so as to bring it at some times closer to the first target and at other times closer to the second target.

20

The method is preferably applied to MSIP, and most preferably CFUBMSIP.

Preferably the movement is rotation of the substrate about an axis. Preferably the axis of rotation does not pass through the substrate.  
25 Alternatively it may pass through the substrate.

An alternative (or addition) is to have moving obstruction means which moves temporarily or periodically to hinder or obstruct or partially hinder or obstruct the deposition of material from one target onto the  
30 substrate to be coated.

The obstruction means may at some times hinder the deposition from one target and at other times hinder the deposition from the other target.

5

The obstruction means may interpose itself in the line of flight of atoms or ions from the target to the substrate to be coated.

According to another aspect of the invention we provide magnetron  
10 sputter apparatus having a first target source of one material and a second target source of a second, different, material, and preferential deposition means adapted to ensure that ions or atoms from one of the sources is preferentially deposited on a substrate to be coated in greater numbers than ions or atoms from the other source, and adjustment means adapted  
15 to vary the ratio of atoms/ions from the first source compared with those from the second source that are deposited on the substrate to be coated.

This can enable a multi-layer structured coating to be achieved.

20 Preferably the preferential deposition means and adjustment means comprise means for moving the substrate to be coated nearer or further from the first and/or second source.

Preferably the preferential deposition means and adjustment means  
25 comprises rotation means adapted to rotate the substrate to be coated about an axis.

Embodiments of the invention will now be described by way of example only with reference to the accompanying drawings of which:-

30

Figure 1 shows a CFUBMSIP system having a target of  $\text{MoS}_2$  and a Titanium target;

Figures 2 and 3 show test results on  $\text{MoS}_2$  coatings;

5

Figures 4 shows schematically an arrangement of first and second magnetron electrode sources side by side;

10

Figures 5A to 5C show schematically possible arrangements of dissimilar source electrodes;

Figure 6 shows another arrangement with three  $\text{MoS}_2$  targets and one titanium target;

15

Figure 7 illustrates another UBMSIP system which has a barrier between two sources; and

20

Figure 8 shows a MSIP system having a reactive metal cleaning target, HLL coating targets, and a gold coating target adapted to produce articles coated with X/Y/X/Y, where X is a HLL material and Y is gold.

Figure 1 shows an unbalanced magnetron sputter ion plating system 10 having a coating or sputter chamber 12, a pumping port 14, a first magnetron 16 having a  $\text{MoS}_2$  target 18, a second magnetron 20 having a titanium target 22, a rotatable component holder 24 holding substrates 26 to be coated, and power supplies 28,30 and 32 for the substrate bias, and first and second magnetrons respectively. There are also two further valved ports 34 and 36 for reactive and non reactive gases respectively.

The preferred deposition method of using the apparatus of Figure 1 is magnetron sputter ion plating and the increase of ion current density produced by using closed field unbalanced magnetron sputter ion plating (UK Patent GB 2 258 343 B) gives improved coating properties. The standard CFUBMSIP is modified and improved by the use of the second target of Ti (or other reactive metal) 30 which is used to getter the impurities in the coating system.

10 The following describes a typical deposition process, which should be taken only as an example.

The chamber, referenced 40, is evacuated to a pressure lower than  $5 \times 10^{-4}$  torr and preferably to lower than  $5 \times 10^{-5}$  torr and then is backfilled with argon gas to a pressure of between  $5 \times 10^{-4}$  torr and  $10^{-2}$  torr and preferably  $2 \times 10^{-3}$  torr. A negative voltage of between 400 and 1000V is applied to the substrates 26 (via the holder 24) and a power of between 50 and 1000W is applied to the titanium target(s) of dimensions 300mmx125mm. Larger targets would require proportionately more power. The substrates are rotated at a speed between 1 and 10rpm.

This ion cleaning stage continues typically for 10 minutes.

For the deposition stage the substrate bias voltage is reduced to a value between floating potential and 75 volts negative and the power to the titanium target(s) is set to a value between zero and 1000W but preferably to 250W and the power to the MoS<sub>2</sub> target(s) is set to about 300W. The power to the MoS<sub>2</sub> targets is not critical and is normally set as high as possible without causing damage to the target. Substrate rotation continues at between 1 and 10rpm during the deposition stage.

Deposition continues typically for between 15 minutes and 60 minutes but if thicker coatings are required the coating period is increased.

Between the ion cleaning and deposition stages as described above  
5 the sequence can be modified to include the deposition of a thin layer of titanium.

During the deposition stage nitrogen can be introduced to the chamber so as to produce  $\text{MoS}_2/\text{TiN}$  coating rather than the  $\text{MoS}_2/\text{Ti}$   
10 coating.

The deposition method used above is, as will be appreciated a standard magnetron sputter method (MSIP) method or a CFUBMSIP method, with the following exceptions:-  
15

During the ion bombardment cleaning of the substrates the titanium sputter target is energised at a low power. For instance using a target size 12" x 4" a target current of between 0.1 and 0.7amps would be used and preferably the current would be 0.1 or 0.2amps. In another example a  
20 current of 2.0amps or 3.0amps also enables the method to work.

During the ion cleaning stage the bias voltage applied to the substrates is sufficiently high to prevent net deposition of titanium onto the substrates and would typically be above 500v negative. The bias  
25 during ion cleaning can be DC, RF, AC, or pulsed DC. The titanium sputtered from the titanium target deposits on the chamber walls and reacts with any water vapour and/or sulphur or other contaminants present in the system to create a clean atmosphere for the ion cleaning and for the subsequent deposition.

The energised titanium magnetron target also serves another purpose in that it allows a discharge to be struck to the biased substrate at a lower gas pressure than would be possible without the energised titanium target. This is because of the effect of the magnetic field of the magnetron. Once the Ti magnetron has been energised its plasma provides electrons and ions which initiate (and maintain) the plasma at the substrate.

Following the ion cleaning stage deposition proceeds in the usual way by energising the MoS<sub>2</sub> magnetron target (or targets) at a power selected to give the required deposition rate (this power is not critical) and if a shutter has been used in front of the MoS<sub>2</sub> target, by opening the shutter. For the deposition the bias voltage on the substrates is reduced from that used during ion cleaning, so that net deposition can take place. The substrates can be earthed, floating or at a bias voltage between the floating voltage and 200 volts negative, but are preferably at a voltage of about 45 volts negative. The bias can be DC, RF, AC or pulsed DC. The bias voltage can be reduced after the power to the titanium target is switched off so that only a MoS<sub>2</sub> layer is deposited. The bias voltage can be reduced before the titanium target is switched off and before the MoS<sub>2</sub> target is energised so that a layer of titanium is deposited prior to the MoS<sub>2</sub> coating. During this stage it is also possible to inlet Nitrogen into the system so that a layer of TiN is deposited prior to the MoS<sub>2</sub> coating.

The titanium target can remain energised during the deposition of the MoS<sub>2</sub> so that a mixture of titanium and MoS<sub>2</sub> is deposited. The titanium content can be between 0 and 40% but preferably would be 10% or less. It is found that the MoS<sub>2</sub>/Titanium mixtures can have as low a coefficient of friction as MoS<sub>2</sub> but with improved mechanical properties and wear resistance.



During this stage it is also possible to maintain a flow of nitrogen gas so that a mixture of Titanium Nitride and  $\text{MoS}_2$  is deposited. The TiN content can be between 0 and 40% but preferably would be 10% or less. It is found that the  $\text{MoS}_2/\text{TiN}$  can have as low a coefficient of friction as  $\text{MoS}_2$  but with improved mechanical properties and wear resistance.

Thus the possible coatings are:-

10

1.  $\text{MoS}_2$  directly on the substrate.
2. A (usually thin) layer of Ti followed by a  $\text{MoS}_2$  coating.
3. A (usually thin) layer of TiN followed by a  $\text{MoS}_2$  coating.
4. A (usually thin) layer of Ti followed by a mixture of  $\text{MoS}_2$  with up to 40% titanium ( $\text{MoS}_2/\text{Ti}$  layer).
5. A (usually thin) layer of TiN followed by a mixture of  $\text{MoS}_2$  with up to 40% TiN ( $\text{MoS}_2/\text{TiN}$  layer).
6. A mixture of  $\text{MoS}_2$  with up to 40% titanium directly on the substrate.
7. A mixture of  $\text{MoS}_2$  with up to 40% TiN directly on the substrate.

15

20

25

In all cases the ion cleaning takes place with the titanium energised.

The titanium in the above description can be replaced with any metal that also getters the impurities to the extent necessary to achieve a significantly improvement performance.

30

The nitrogen in the above description can be replaced with oxygen or a hydrocarbon gas or mixtures of these gases.

- 5        The substrate in the above description can be of any material and can include a substrate already coated with another material.

10        The  $\text{MoS}_2$  or  $\text{MoS}_2/\text{Ti}$  or  $\text{MoS}_2/\text{TiN}$  coatings can have thicknesses from very thin,  $0.1\mu\text{m}$  or less to very thick,  $10\mu\text{m}$  or more, but would preferably be about  $1\mu\text{m}$ . The very thin coatings still give good performance because of the high wear resistance of the coatings. The very thick coatings are useful because the wear rate is approximately uniform throughout the thickness of the coating and therefore they can give very long lives. This is totally unlike  $\text{MoS}_2$  deposited by earlier  
15        methods where most of the thickness of thick coatings would wear away very quickly and only the last thin coating, about  $0.25\mu\text{m}$ , would provide any useful, wear resistance.

20        The  $\text{MoS}_2$  deposited as described above has very good tribological properties, with significant improvements over previous  $\text{MoS}_2$  coatings.

If the  $\text{MoS}_2$  is co-deposited with Ti or TiN as described above the tribological properties are further improved.

- 25        The co-deposited coatings can be deposited by simultaneous deposition from a  $\text{MoS}_2$  target and a neighbouring titanium target to produce a coating consisting of a mixture of  $\text{MoS}_2$  and Ti (or TiN). (See Figure 4). There may be an ion cleaning titanium target and a separate co-depositing titanium target, or they may be the same target.

Alternatively and preferably the coatings can be deposited in a typical Closed Field Unbalanced Magnetron Sputter Ion Plating System (UK Patent GB 2 258 343 B) in which the substrates are rotated between magnetrons mounted around the substrate rotation axis.

5

Three possible arrangements are shown in Figures 5a to 5c. A fourth arrangement is shown in Figure 6.

With the arrangement of Figures 5a to 5c or Figure 6 the coating  
10 will not consist of a uniform mixture of  $\text{MoS}_2$  and Ti but will consist of a layered structure A/B/A/B/A/B/A etc where A is rich in Ti and B is rich in  $\text{MoS}_2$ .

A can be 100%  $\text{MoS}_2$  and will usually be more than 50%  $\text{MoS}_2$ . B  
15 can be 100% Ti and will usually be more than 50% Ti.

It is this type of layered structure that gives the best tribological properties.

20

The period (ie the double layer thickness) is defined by the powers applied to the targets and the rotational speed. Normally the maximum safe power is applied to the  $\text{MoS}_2$  target (or targets) in order to obtain the maximum deposition rate. The maximum safe power is normally about 250W on a 300mm x 125mm target. Although higher powers are possible  
25 they can cause cracking in the rather brittle  $\text{MoS}_2$  target. Therefore it is usual to leave the  $\text{MoS}_2$  power constant and the thickness of the double layer is defined by the rotational speed. The period can vary from very thin, which approximates to a homogeneous mixture, and which is obtained at fast rotational speeds, ie faster than 10rpm., up to a period

greater than 1000 Å but preferably the period is between 30 Å and 200 Å with the best results obtained at a period of about 80 Å.

The choice of ratio of thickness  $\text{MoS}_2/\text{Ti}$  and the optimum ratio  
5 depends on the period.

For a large period a higher  $\text{MoS}_2/\text{Ti}$  ratio is preferable. For a period of 80 Å the  $\text{MoS}_2/\text{Ti}$  thickness ratio is normally between 5/1 and 1/1.

10

It has been found that the coatings produced by the above described methods have a coefficient of friction consistently below 0.1 and frequently as low as 0.02.

15

There may be more than one "second" target. They need not necessarily be of the same metal.

It will be appreciated that in the foregoing we could have more than one metal sulphide source (e.g. more than one  $\text{MoS}_2$  source or, for  
20 example, we could have one  $\text{MoS}_2$  source and one  $\text{WS}_2$  source). We could have more than one metal source (e.g. more than one Ti source, or a source of one metal and another source of a different metal).

Whilst it might theoretically be possible to replace the  $\text{MoS}_2$  (or the  
25 like) source with uncompounded sources of the elements we are not aware of such a system working and we would envisage having one or more metal-sulphur compound sources.

We have used the UBMSIP system described in UK Patent  
30 GB 2 258 343 B to produce very good coatings of  $\text{MoS}_2$ . We believe that

the high ion content density at the substrate to be coated (greater than  $1\text{mA}/\text{cm}^2$ ) and the low bias voltage of the substrate to be coated (typically 45 V negative) are factors in the production of good coatings, but they may not be essential. The coating is adherent and has a dense coherent structure. The general tribological properties are extremely good and the coatings also give improved cutting tool performance for several work piece materials, and allow high speed machining, unlubricated or with minimal lubrication.

10 We coated a high speed steel plate with  $\text{MoS}_2$  using our system, with about 10% Titanium in the structure and the results of tests on the coated workpiece are given below:

15 coefficient of friction: generally 0.02. This is very low indeed. Humidity has only a slight effect on the friction.

Adhesion: The critical load  $L_c$  was greater than 70N. This is very high.

20 Hardness: Vickers Microhardness Tests indicate a hardness of over 500Hv. This very high figure is confirmed by Nano Indentation tests.

25 Wear Resistance: The extreme wear resistance is indicated by ball on disc test results, using a 6mm steel ball, a load of 80N and a linear speed of 5000mm/min. Typically a  $1\mu\text{m}$  thick coating of  $\text{MoS}_2$  on a tool steel substrate is not removed after 3 hours of running.

30

Figures 2 and 3 show a comparison with some prior art  $\text{MoS}_2$  coatings we have produced. The tests were performed using a Teer ST-2200 reciprocating tester. The load was 100N on a 5mm diameter WC-Co ball. The speed was 150mm/sec with a half period of 1 sec.

It will be seen from Figures 2 and 3 that the life of the coating is considerably more what we could achieve before the present invention.

Tests also show an improvement in cutting tool performance when they are coated with our new  $\text{MoS}_2$  coating. Drilling tests into Al 15% Si alloys give a life of uncoated drills of about 50 holes. The same HSS drills coated with our  $\text{MoS}_2/\text{Ti}$  coating produced over 700 holes without failure.

15

Many tests have been carried out on carbide cutting tools coated with  $\text{TiN}$ ,  $\text{TiAlN}$  or other hard coatings followed by a  $\text{MoS}_2$  coating. The work piece materials that were machined included cast iron, stainless steel, Al alloys, Mg alloys, and Nickel based alloys. Our  $\text{MoS}_2$  coatings produced an improvement in life of at least a factor of two, but in many cases the improvement was even greater.

20

Significant improvements in performance have been recorded on drills, milling cutters, reamers, saw blades, and turning tools.

25

Similar improvements have found in relation to forming tools, such as dies and punches.

Improvements have been found in other components such as bearings, gears, automobile engine components, control valves, and other general machine parts.

5        Our MoS<sub>2</sub> coatings which have the properties described above are believed to be new and inventive in their own right. They may have a Titanium, or other metal, content. The other metal content may be 0%, ½%, 1%, 1½, 2%, 2½%, 3%, 3½, 4%, 5% or higher (by percent of number of atoms in the coating layer). The metal content may be 30%  
10       or less, or 10% or less for MoS<sub>2</sub>/Ti or MoS<sub>2</sub>/TiN coatings.

We can produce coatings that have a critical adhesion load of at least 50N, 60N, or at least 70N. The coefficient of friction may be 0.05 or less, or 0.02 or less. The Vickers hardness may be 500HV or more.  
15

We have discovered a further inventive feature. Our MoS<sub>2</sub> coating deposited in a typical CFUMSIP system with substrate rotation is surprisingly hard - about 500 Vickers. This is harder than stainless steel. MoS<sub>2</sub> coatings have previously been soft - it was possible to scratch them  
20       off with a fingernail. Our coatings deposited with the CFUMSIP system with substrate rotation have a multi-layer structure: Ti/MoS<sub>2</sub>/Ti/MoS<sub>2</sub>/Ti/MoS<sub>2</sub>/Ti/MoS<sub>2</sub> etc. (The MoS<sub>2</sub> layers may still have traces of Titanium in them). It is well known that multi-layer structures can be much harder than homogenous structures.

25

Our coating may have a plurality of layers of hexagonal layer lattice material (HLL material). There may be a series of layers of one or more HLL material(s) and a series of layers of one or more hard (e.g. metal, or carbon, or Diamond-like carbon) materials, with the two series

of layers being alternatively interlaced. Preferably there are many (e.g. 3, 4, 5 or more) layers of HLL material.

When we energise both magnetron electrodes at once (the Titanium and the MoS<sub>2</sub>) we have a rotating component holder between them. A sample situated on the component holder cycles itself closer to the Titanium source, equidistant from both Titanium and MoS<sub>2</sub> source, closer to the MoS<sub>2</sub> source, equidistant from both sources, and so on. When it is closest to the titanium source it has a layer rich in Titanium deposited on it. When it is closest to the MoS<sub>2</sub> source it has a layer rich in MoS<sub>2</sub> deposited on it.

A similar effect may be achieved by switching the Titanium and MoS<sub>2</sub> sources on and off in sequence (possibly fading them on or off (or both) so that their energisations overlap in time to provide a "blending" of the layers, avoiding too sharp a change). Alternatively we may prefer to have a sharp layer boundary.

Figure 7 illustrates a modified UBMSIP system which has a barrier member, or dividing member, that masks one side of the component holder (at any instant) from the effects of one of the magnetron ion sources. This accentuates the layering effect of the coating process. the power to the magnetrons may also be varied, or may be left constant. If the holder has several articles to be coated angularly distributed around it the power would normally not be varied during the main coating process (of course during their cleaning it would be varied - Titanium on, MoS<sub>2</sub> off).

We may have a third or further electrode(s)/magnetron(s) to provide a third (or further) layer, possibly of another metal or alloy. The



third (or further) magnetron may have a metal or carbon (or metallic semi-metal) target, or a compound (eg N.C. or O compound). The mask/barrier member (if provided) may define three (or more) compartments.

5

We may have a gettering electrode, a first coating material electrode and a second coating material electrode.

We prefer to have three  $\text{MoS}_2$  electrodes and one Titanium  
10 electrode in a 4 magnetron UBMSIP system, with the magnetrons in the closed field arrangement as described in UK Patent GB 2 258 343 B.

The rotation rate of the component holder can be varied to vary the thickness of the individual layers.

15

Instead of Titanium we may use another reactive metal, such as vanadium, chromium, zirconium, niobium, molybdenum, tantalum, hafnium, or tungsten or an unreactive metal, such as gold or platinum.

20

It will be appreciated that a non-reactive metal will not work for the ion cleaning of the system, but can be used during the deposition (in addition to or, instead of the reactive metal).

Figure 8 illustrates a MSIP system, which will usually use  
25 unbalanced magnetrons, in which there is a reactive metal target (e.g. titanium), two hexagonal layer lattice targets (e.g.  $\text{MoS}_2$ ), and a non-reactive metal target (e.g. gold). The substrate to be coated is rotated by a component holder. The system would preferably be a closed field system (U.K. Patent GB 2 258 343 B)

30

The reactive metal target is energised in the ion cleaning operation of the system to clean the system by producing gettering ions or neutrals which mop up impurities. During the coating operation there are different ways that the system can be operated.

5

One way is to energise the HLL targets (e.g.  $\text{MoS}_2$ ) and the other metal target (e.g. Au) to produce a coating X/Y/X/Y/X/Y etc where X is a HLL layer and Y is a non-reactive metal layer (or vice-versa). Such a coating has been found to have good hardness and tribological properties.

10 It will be noted that the reactive target is needed to produce a clean environment but in the mode of operation described does not provide coating material.

A second mode of operation has the reactive metal target energised  
15 during the coating operation to produce coatings of X/Y/X/Y/X/Y etc where X is a HLL material and Y is a metal/Ti mixture (or vice-versa).

It is possible to produce X/Y/Z/X/Y/Z etc coatings where X is HLL material, Y is reactive metal (or non-reactive metal), and X is non-  
20 reactive metal (or reactive metal). We could, of course, have a fourth target, or subsequent targets, of different material to give the capability of depositing a layer with a content of the fourth or further targets. We could use such a multi-target system to deposit different coatings at different times.

25

Platinum is another non-reactive metal that gives good coating results.

Instead of, or in addition to the gold (or other non-reactive metal) target we may have a carbon target (or other "metallic" non-metal) and produce layered coatings having carbon layers.

- 5        The carbon layer may be deposited as diamond-like carbon. Such multi-layer coatings have also been found to have good hardness, adhesion, and low friction.

- 10       Instead of  $\text{MoS}_2$  we may use any hexagonal layer/lattice material eg  $\text{WS}_2$  or  $\text{TiS}_2$ . We may use  $\text{NbS}_2$ ,  $\text{TaS}_2$ ,  $\text{MoSe}_2$ ,  $\text{NbSe}_2$ ,  $\text{TaSe}_2$ ,  $\text{MoTe}_2$ ,  $\text{NbTe}_2$ ,  $\text{TaTe}_2$  or  $\text{WTe}_2$ , or mixed compounds of any of the foregoing.

- 15       The coatings that we make may have a stoichiometric ratio of metal to non-metal (e.g. in  $\text{MoS}_2$ ), or a non-stoichiometric ratio. We may produce a coating with less non-metal in it than the stoichiometric ratio (a sub-stoichiometric composition).

- 20       For example a molybdenum sulphur coating may be  $\text{MoS}_2$  at the stoichiometric ratio or  $\text{MoS}_x$  where x is above or below two. "X" may be about 1.5. X may be from 1.2 to 2.5.

Even if the target of  $\text{MoS}_2$  is stoichiometric the coating need not be. We can get a variety of sub stoichiometric coatings in tests.

- 25       Thus where in the protection - defining claims of this application we refer to  $\text{MoS}_2$  we mean molybdenum/sulphur composition having a hexagonal layer lattice structure (or substantially one) and having stoichiometric or non-stoichiometric composition.

It will be appreciated that the heart of the cleaning process is that during a normal deposition sequence the surfaces of the substrates are cleaning by ion bombardment. The ions are produced by applying a high (typically 1000V) negative bias to the substrates in an atmosphere of argon gas at a pressure of about  $2 \times 10^{-3}$  torr. The argon ion bombardment is aided here by the operation of the second electrode which produces a flux of reactive metal into the chamber and which removes contaminants from the atmosphere in the chamber. We bombard the substrates using argon ions as in a conventional process, and the reactive metal flux from the 2nd electrode is cleaning up the atmosphere in this process and thus making it more effective.

## CLAIMS

1. A sputter ion plating system having a first target of metal sulphide (e.g.  $\text{MoS}_2$  or  $\text{WS}_2$ ) and a second target of metal.
- 5 2. A sputter ion plating system according to claim 1 in which the first target is a metal disulphide.
3. A sputter ion plating system according to claim 1 or claim 2 in  
10 which the metal second target is made of titanium, or any one of: vanadium, chromium, zirconium, niobium, molybdenum, tantalum, hafnium, or tungsten (referred to as "reactive metals").
4. A sputter ion plating system according to any preceding claim in  
15 which the first and second targets are each separately energisable (e.g. each have their own associated and independent power supply).
5. A sputter ion plating system according to any preceding claim  
20 which is capable of being activated in a cleaning operation in which the second target is energised.
6. A sputter ion plating system according to claim 5 in which the first (e.g.  $\text{MoS}_2$ ) target can be energised but is adapted not to be energised during the ion cleaning operation.
- 25 7. A sputter ion plating system according to any preceding claim in which the first target comprises a magnetron with a target element.
8. A sputter ion plating system according to any preceding claim in  
30 which the second target comprises a magnetron with a target element.

9. A sputter ion plating system according to claim 7 or claim 8 in which the magnetron of the first or second target (and preferably the magnetrons of both the first and second targets) is unbalanced.

5

10. A sputter ion plating system according to any preceding claim which is a magnetron sputter ion plating system using unbalanced first and second magnetrons associated with the first and second targets respectively.

10

11. A method of improving the sputter deposition of  $\text{MoS}_2$  coatings comprising operating a sputter ion plating system in cleaning operation prior to a coating operation, the sputter system having a first target of material to be coated onto a substrate, and a second, cleaning, target of metal, and in which in the cleaning operation the second target is energised to produce a flux of reactive cleaning metal which reacts with impurities in the sputter chamber so as to remove them from having an active presence during the ion bombardment cleaning of the substrate and subsequent coating operation in which the first target is energised.

20

12. A method according to claim 11 in which at least some of the reactive cleaning metal is ionised metal.

13. A method according to claim 11 in which the reactive cleaning metal is a sputtered, unionised, metal.

25

14. A method according to any one of claims 11 to 13 in which the second target is titanium, or another reactive metal.

15. A method according to any one of claims 11 to 14 in which the first and/or second targets have a respective associated magnetron.

16. A method according to any one of claims 11 to 15 which is practised in a magnetron sputter Ion Plating system which is adapted to operate in use such that the cleaning operation involves the bombardment of the substrates to be coated by ions and also involves the bombardment of the second target with ions so as to create metal ions or sputtered atoms from the second target in the sputter chamber, the metal ions or sputtered atoms cleaning the walls of the chamber and reacting with impurities in the atmosphere of the chamber so as to remove the impurities from the system.

17. A method according to any one of claims 11 to 16 in which water and/or sulphur in the sputter chamber atmosphere react with the metal, preferably titanium or another reactive metal, created from the second target to form stable and non-contaminating compounds during the cleaning operation.

18. A method according to any one of claims 11 to 17 which includes the step of introducing to the sputter chamber in the coating operation a further material which is incorporated in the coating.

19. A method according to claim 18 in which the further material is gaseous at its point of introduction, and may be nitrogen, or oxygen, or a hydrocarbon gas.

20. A method according to any one of claims 11 to 19 which further comprises the steps of laying down a layer of titanium (or other reactive metal) followed by a layer of molybdenum disulphide (or other HLL

material), or by a layer of molybdenum disulphide/titanium mixture (or other HLL material/Ti mixture).

21. A method according to any one of claims 11 to 20 further  
5 comprising laying down a layer of titanium (or other reactive metal) nitride followed by a layer of molybdenum disulphide (or other HLL material) or a layer of molybdenum disulphide (other HLL material)/titanium (or other reactive metal) nitride mixture.

10 22. A method according to any one of claims 11 to 21 in which the coating is between  $0.1\mu\text{m}$  and  $10\mu\text{m}$  thick, preferably about  $1\mu\text{m}$  thick.

23. - An article coated using the system of any one of claims 1 to 10 or using the method of any one of claims 11 to 22.

15

24. An article according to claim 23 which has a coating of a mixture of  $\text{MoS}_2/\text{Ti}$ , or  $\text{MoS}_2/\text{TiN}$ .

25. An article according to claim 24 in which the  $\text{MoS}_2/\text{Ti}$ , or  
20  $\text{MoS}_2/\text{TiN}$ , coating has a Ti, TiN, content of 10% or less, or 30% or less (by % of those atoms/compounds in the total number of atoms of the coating - atomic percent).

26. An article according to any one of claims 23 to 25 in which the  
25 basal planes of the metal sulphide layer (e.g.  $\text{MoS}_2$ ) are parallel, or substantially parallel, to the surface of the substrate that they coat.

27. The use of second target of metal in a cleaning operation of a  
sputter ion plating system so as to reduce or eliminate impurities in a low-  
30 friction coating subsequently produced from the system.



28. The use of a second target of metal according to claim 27 in a MSIP system.
- 5 29. The use of a second target of metal according to claim 27 or claim 28 in which the impurities being reduced or eliminated are caused by water or sulphur.
- 10 30. The use of a second metal target in a cleaning operation of a sputter ion plating system for the production of a low friction metal-sulphur, e.g.  $\text{MoS}_2$ , coating with improved mechanical properties.
31. The use of a second metal target in accordance with claim 30 in a MSIP system.
- 15 32. Magnetron sputter ion plating apparatus having a first target source of one material and a second target source of a second, different, material, and preferential deposition means adapted to ensure that ions or atoms from one of the sources are preferentially deposited on a substrate
- 20 to be coated in greater numbers than ions or atoms from the other source, and adjustment means adapted to vary the ratio of atoms/ions from the first source compared with those from the second source that are deposited on the substrate to be coated, the arrangement being such that the apparatus is capable of producing a multi-layer structured coating.
- 25 33. Apparatus according to claim 32, in which the preferential deposition means and adjustment means comprise means for moving the substrate to be coated nearer or further from the first and/or second source.

34. Apparatus according to claim 33 in which the preferential deposition means and adjustment means comprises rotation means adapted to rotate the substrate to be coated about an axis.

5 35. Magnetron sputter ion plating apparatus substantially as described with reference to any of the accompanying drawings.

36. A method of achieving in a magnetron sputter ion plating apparatus a layered coating having layers of a first kind and layers of a, different,  
10 second kind, the method comprising having a first target source of one material and a second target source of a second material and moving the substrate to be coated so as to vary its distance from the first and second targets so as to bring it at some times closer to the first target and at other times closer to the second target.

15

37. A method according to claim 36 which comprises rotating the substrate to be coated about an axis.

38. A method according to claim 36 or claim 37 in which the axis of  
20 rotation does not pass through the substrate.

39. A method of achieving in a magnetron sputter ion plating apparatus a layered coating having layers of a first kind and layers of a second, different, kind substantially as described herein.

25

40. An article having a coating of hexagonal layer lattice material (eg  $\text{MoS}_2$ ) in which the article has a coated surface area and in which the basal planes of the hexagonal layer lattice material are generally parallel with the coated surface area, at least in the region where they overlie said  
30 coated surface area.

41. An article having a multi-layer coating X/X/X/Y etc where X is one of i) a layer of hexagonal layer lattice material, or ii) a layer of metal (reactive metal or non-reactive metal) or semi-metal (eg carbon), or a mixture or alloy having in it a metal or semi-metal; and where Y is the other of i) or ii).
42. An article according to claim 40 or 41 in which coating is a low friction coating and the hexagonal layer lattice material is a metal sulphide.
43. An article according to claim 42 in which the metal sulphide has a composition of Me (metal) to sulphide of  $\text{MeS}_x$ , where x is from 1.2 to 2.5.
44. An article according to claim 43 in which x is about 1.5.
45. An article according to claim 43 in which x is about 2.
46. An article according to any one of claims 40 to 45 in which the coating has an adhesive critical load of at least 50 or 60N.
47. An article according to claim 46 in which the critical load for the coating adhesion is at least 70N.
48. An article according to any one of claims 40 to 47 in which the coating has a coefficient of friction of 0.05 or less.
49. An article according to claim 48 in which the coefficient of friction is about 0.02, or less.

50. An article according to any one of claims 40 to 49 in which the coating has a Vickers hardness of 500Hv or more.
- 5 51. An article according to any one of claims 40 to 50 in which the coating comprises a substantially homogeneous mixture of HLL material and metal (or semi-metal).
52. An article according to any one of claims 40 to 50 in which the  
10 coating is not a homogeneous layer but instead has layers of different composition: one kind of layer comprising HLL material and another kind of layer comprising metal (or semi-metal), the two sets of layers alternating.
- 15 53. An article with a coating substantially as described herein.
54. A method of producing coatings having a hexagonal layer lattice layer substantially as described herein with reference to any of the accompanying drawings.



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Claims searched: 1-31, in part 53, & in part Date of search: 26 September 1996  
54

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

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Other: Online: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2228268 A (PIONEER) see esp p9 lines 3-22 & fig 2	1 at least
X	GB 2199593 A (EVANS) see esp p6 lines 17-28	1 at least
X	EP 0409451 A1 (OPTICAL) see esp exs	1 at least
X	EP 0198459 A2 (HITACHI) see esp p9 line 24 - p10 line 12	1 at least
X	WO 92/01081 A1 (BOC) see esp p16 lines 15-26	1 at least
X	WO 91/14797 A1 (TEER) see whole doc	1 at least
X	US 5282985 (ZABINSKI) see esp col 1 lines 43-51; col 2 line 65 - col 4 line 5	1 at least
X	US 5196105 (LEYBOLD) see esp col 3 line 54 - col 4 line 12; col 6 lines 39-68 & figs	1 at least
X	US 4731172 (MATSUSHITA) see esp col 2 lines 10-39 & fig 1	1 at least
X	US 4704301 (IBM) see esp col 5 line 28-39; col 6 lines 37-60 & figs	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



# The Patent Office

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**Application No:** GB 9615137.8  
**Claims searched:** 1-31, in part 53, & in part 54  
**Examiner:** Peter Beddoe  
**Date of search:** 26 September 1996

Category	Identity of document and relevant passage	Relevant to claims
X	Patent Abstracts of Japan vol 15, no 130 (E-1051) 4658 page 61 & JP 314227 A (SHARP) see abstract	1 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.